Study on solvent and process simulation for CO2 absorption

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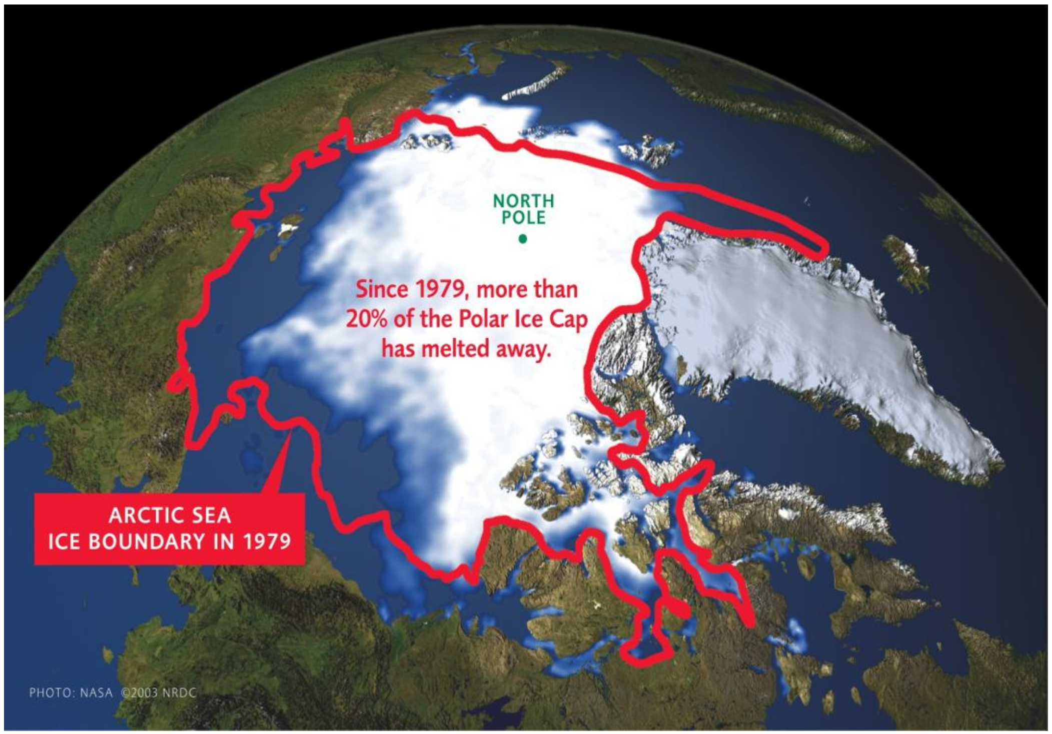
Contents

Background-Global Warming Issue



Since 1979, more than 20% of the Polar ice Cap has melted away(2005)

Background- Importance of CCS

- **CO_2 is the main part of greenhouse gases**

- **Methods to lower CO_2 emission:**

  energy saving, energy constitution

  capture and sequestration

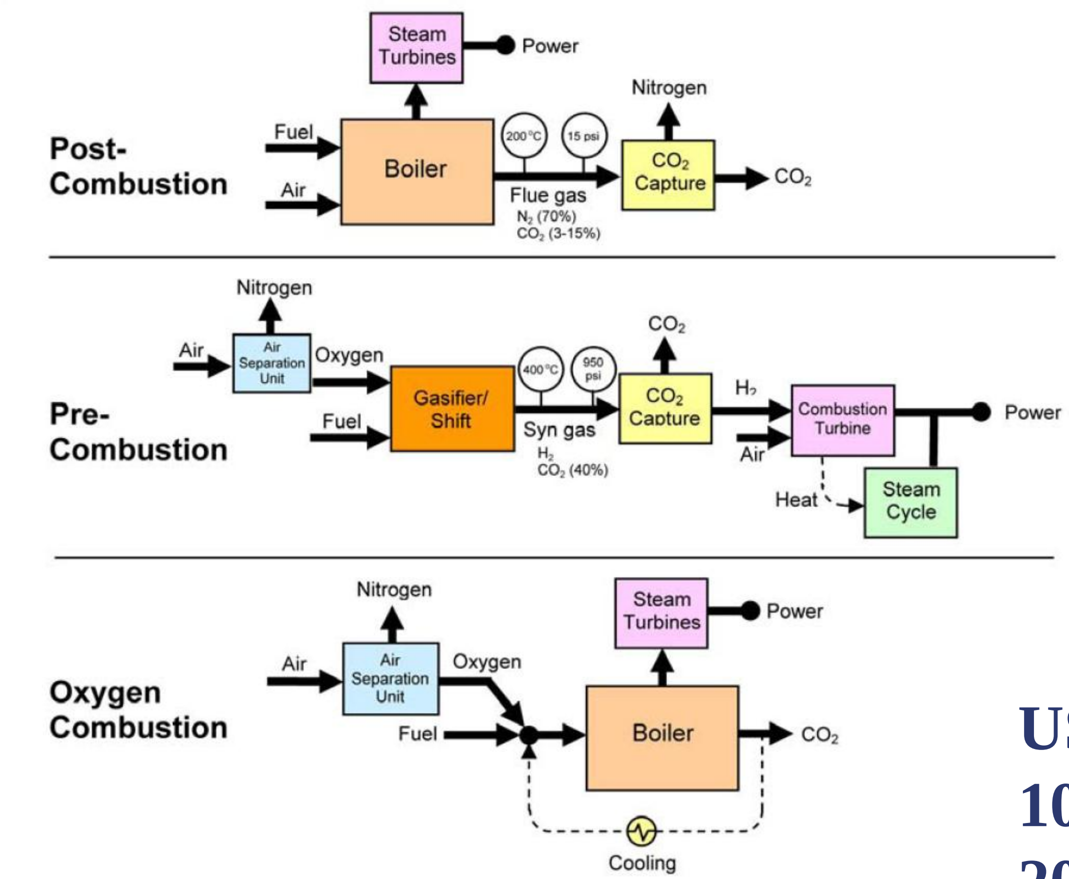
- **CO_2 is mainly from fossil energy resources**

  Science,“Ready for CCS”, 2007,2.

  US、Russia、China、India and Australia, 75%

- **CCS cost < disasters because of CO_2 emission**

Background- Cost of CCS

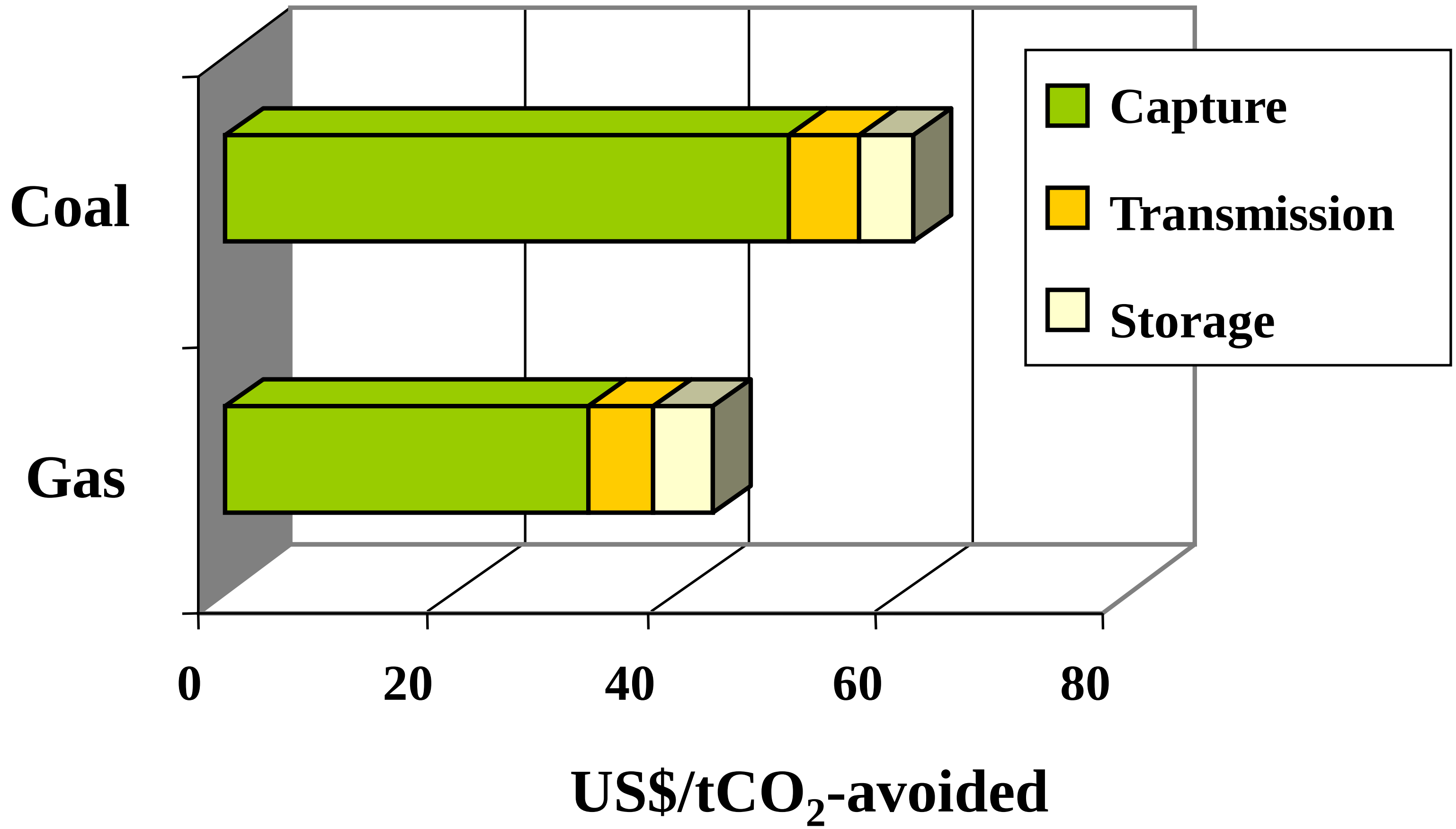


30-50$ / tCO2,
25-35% ↓ in kWh
30-50% ↑ in e p

20-25$ / tCO2,
5-10% ↓ in kWh
20-30% ↑ in e p

US Routine, 2012:
10% pre-combustion
20% post-combustion

Background-Cost of CCS



Cost relative to use of same fuel in least cost plant without capture

Source: International Energy Agency

Background - CO_2 capture methods

- **Absorption**

  Chemical, low-pressure, high energy consumption

  MEA,DEA,MDEA, AMP

  Physical, high-pressure, low energy consumption

  Methanol, Propylene carbonate, Polyethanol Glycol

- **Membrane CO_2/H_2, CO_2/N_2**

- **Adsorption, high-pressure**

Background - Main research topics

- **Study on molecular design for solvents**

  higher absorption ability for CO_2, lower energy consumption for solvent regeneration. Structure ←→absorption ability

- **Study on mass transfer packings**

  Improve mass transfer efficiency, lower cost on facility and operation.

- **Study on process simulation**

  Pursue new processes，lower total capture cost.

Contents

Absorption solvents

For CO2 solubility in aqueous amine solution

Vapor-liquid equilibrium with Chemical Reactions:

Dissociation of water	$H_2O \Leftrightarrow OH^- + H^+$
First grade hydrolysis of CO_2	$CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+$
Second grade hydrolysis of CO_2	$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$
Protonation of an Amine	$AmineH^+ \Leftrightarrow Amine + H^+$
Formation of a Carbarmate	$Amine + CO2 \Leftrightarrow AmineCOO^- + H^+$

Absorption Solvents

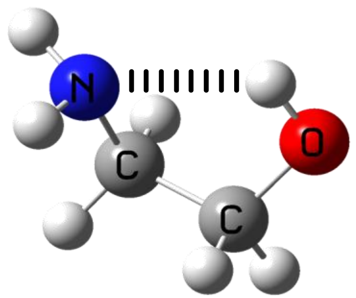
Chemical Solvents and their properties

Solvents		Circle Loading	Rate	Degradation
Primary,	MEA	0.25	Fast	Middle
Secondary,	DEA	0.3	Middle	Middle
Tertiary,	MDEA	0.3	Slow	Slow
Steric Hindered,	AMP	0.6	Slow	Middle+

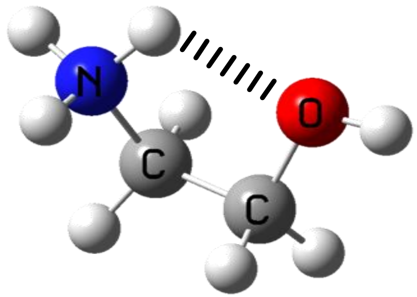
Mixing Solvents for best loading and rate:

AMP/MEA， MDEA/PZ

Molecular design for solvents



Monoethanolamine



Monoethanolamine(H^+)

$$A_{aq} + H^+_{aq} \Leftrightarrow AH^+_{aq}$$

$$\begin{array}{ccc}
A_{gas} + H^+_{gas} & \xrightarrow{\Delta G_{gas}} & AH^+_{gas} \\
\Delta G_{sol}(A)\downarrow \quad \downarrow \Delta G_{sol}(H^+) & & \downarrow \Delta G_{sol}(AH^+) \\
A_{aq} + H^+_{aq} & \xrightarrow{\Delta G_{aq}} & AH^+_{aq}
\end{array}$$

Wei Chen, et al. 11th International Conference on Properties and Phase Equilibria for Product and Process Design. May 20-25, 2007. Crete, Greece.

Calculation of Reaction Gibbs energy

Table 1. Gas-Phase Energies ΔG_{gas} (kcal/mol)

	$\Delta G_{gas}{}^{a}$	$\Delta G_{gas}{}^{b}$	$\Delta G_{gas}{}^{c}$	$\Delta G_{exptl}{}^{d}$
MEA	-212.39	-212.30	-211.87	-214.34
DEA	-224.26	-223.97	-223.22	-219.88
MDEA	-226.98	-227.18	-225.38	
2-(methylamino)ethanol	-219.26	-219.16	-218.71	
1-amino-2-propanol	-214.24	-214.16	-213.35	

[a] B3LYP/6-311+G(3df,2p)//HF/6-31+G(d), the zero-point energy and thermal correction scaled by 0.8929.

[b] B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d), the zero-point energy and thermal correction scaled by 0.9804.

[c] CBS-4. [d] Experimental data taken from ref 27.

Calculation of Reaction Gibbs energy

Table 2. Solvation Energies $\Delta G_{sol}(AH^+)-\Delta G_{sol}(A)$ (kcal/mol)

	CPCM[a]	CPCM[b]	CPCM[c]	CPCM[d]
MEA	-60.61	-60.88	-60.56	-60.72
DEA	-51.38	-51.71	-51.25	-51.42
MDEA	-47.22	-47.80	-48.09	-47.62
2-(methylamino)ethanol	-56.14	-56.40	-56.14	-56.20
1-amino-2-propanol	-59.29	-59.44	-59.00	-59.26

[a] CPCM/HF/6-31+G(d)//HF/6-31+G(d). [b] CPCM/B3LYP/6-31+G(d)//HF/6-31+G(d).

[c] CPCM/B3LYP/6-31+G(d)//B3LYP/6-31+G(d). [d] CPCM/B3PW91/6-31+G(d)//HF/6-31+G(d).

Calculation of Reaction Gibbs energy

Table 3. pK_a Values in Aqueous Solution

	B3LYP/6-311+G(3df,2p)//HF/6-31+G(d)		CBS-4		
	CPCM[a]	CPCM[b]	CPCM[a]	CPCM[b]	
	pK_a	pK_a	pK_a	pK_a	p$K_{a(exptl)}$[c]
MEA	-8.51	-8.71	-8.13	-8.33	-9.51
DEA	-10.44	-10.69	-9.68	-9.93	-8.95
MDEA	-9.39	-9.82	-8.22	-8.64	-8.63
2-(methylamino)ethanol	-10.27	-10.46	-9.87	-10.06	-9.77
1-amino-2-propanol	-8.90	-9.01	-8.25	-8.36	-9.46

[a] CPCM/HF/6-31+G(d)//HF/6-31+G(d). [b] CPCM/B3LYP/6-31+G(d)//HF/6-31+G(d). [c] Experimental data taken from ref 32.

Calculation of Reaction Gibbs energy

Table 4. Hydrogen Bond Lengths (*L*)

	bond	L (Å)[a]
MEA	H(O)···N	2.251
$MEAH^+$	H(N)···O	2.051
DEA	H(O1)···N	2.276
	H(N)···O2	2.432
$DEAH^+$	H1(N)···O1	2.086
	H2(N)···O2	2.086
MDEA	H(O1)···N	2.402
	H(O2)···N	2.402
$MDEAH^+$	H(N)···O1	2.156
	H(N)···O2	2.156
2-(methylamino)ethanol	H(O)···N	2.285
2-(methylamino)ethanol(H^+)	H(N)···O	2.068
1-amino-2-propanol	H(O)···N	2.187
1-amino-2-propanol(H^+)	H(N)···O	2.018

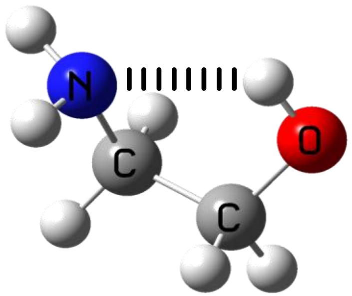
[a] Most stable geometry optimized at the B3LYP/6-31+G(d) level.

The effect of a hydrogen bond

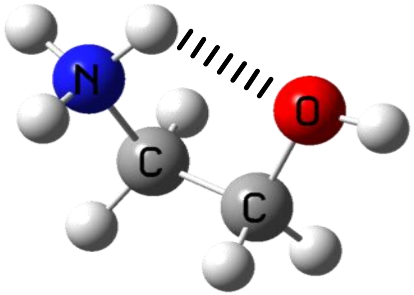
- With no hydrogen bond for MEA in water, the result is improved as:

  13.48   13.75   12.96 13.23
  compared with 12.97

- With no hydrogen bond for DEAH+ in water, the result is improved also clearly.



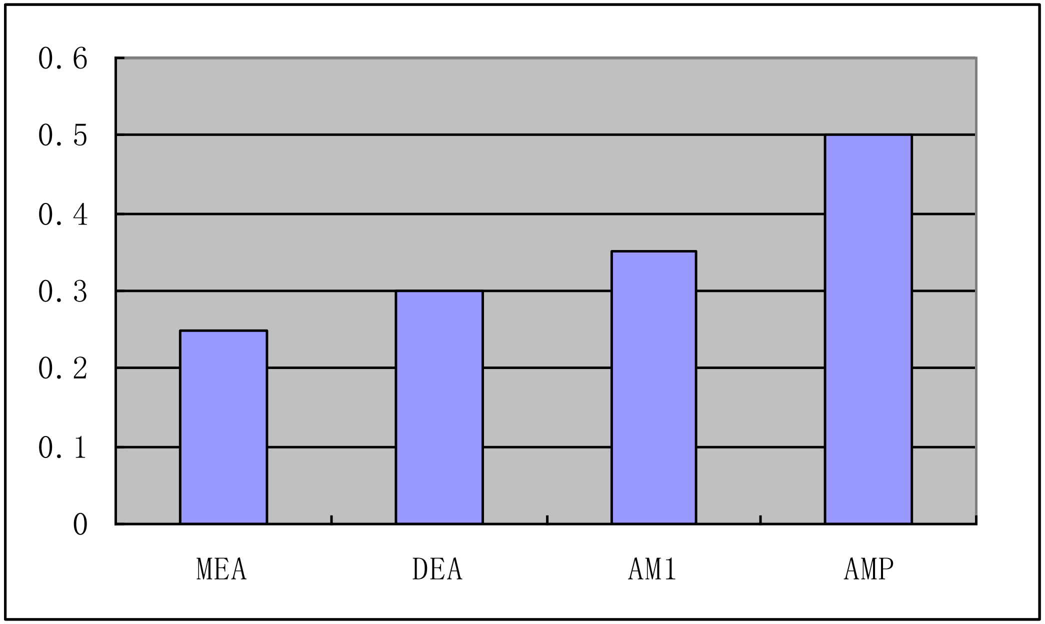
Monoethanolamine



Monoethanolamine(H^+)

Loading of different absorption solvents

Molecular Structure ←→ Capture Ability



Circulation Loading of absorption solvents

Contents

Study on mass transfer packings

High efficient packings:

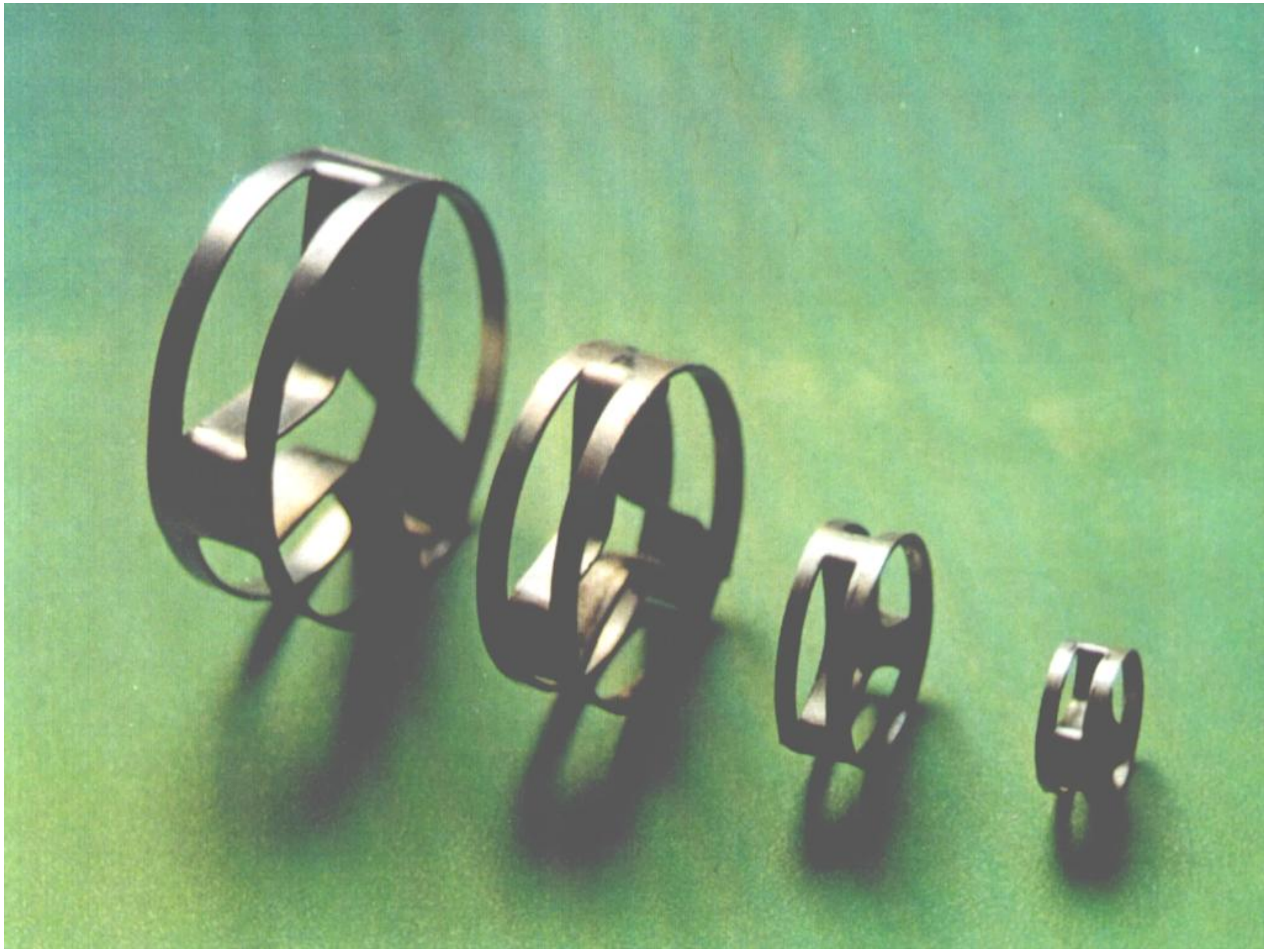
Faster mass transfer
Lower packing height

Lower pressure drop
Lower pumping energy

CFD Simulation

Pall Ring

Super Mini Ring(SMR)

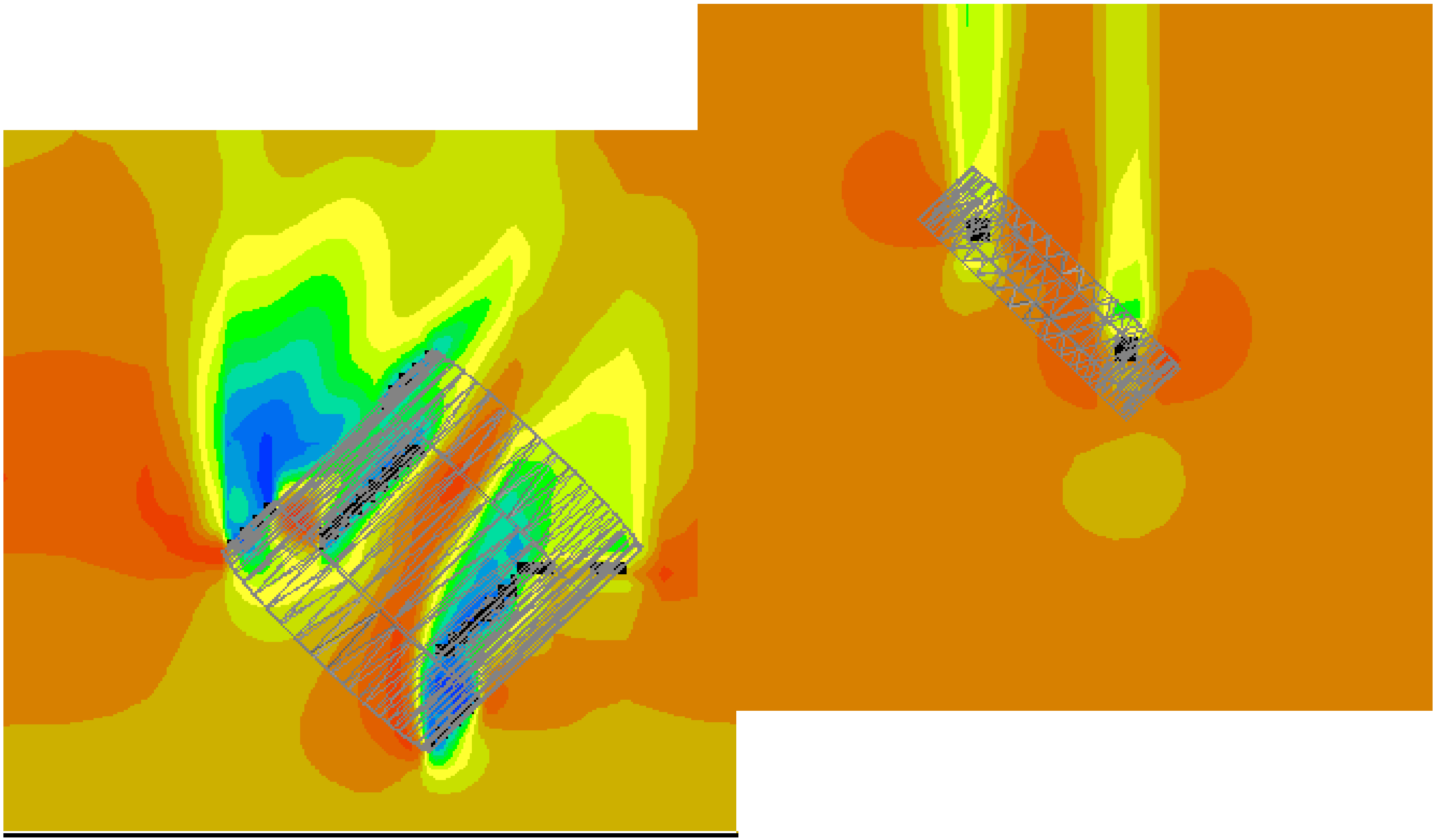


Computational Fluid Dynamics (CFD)

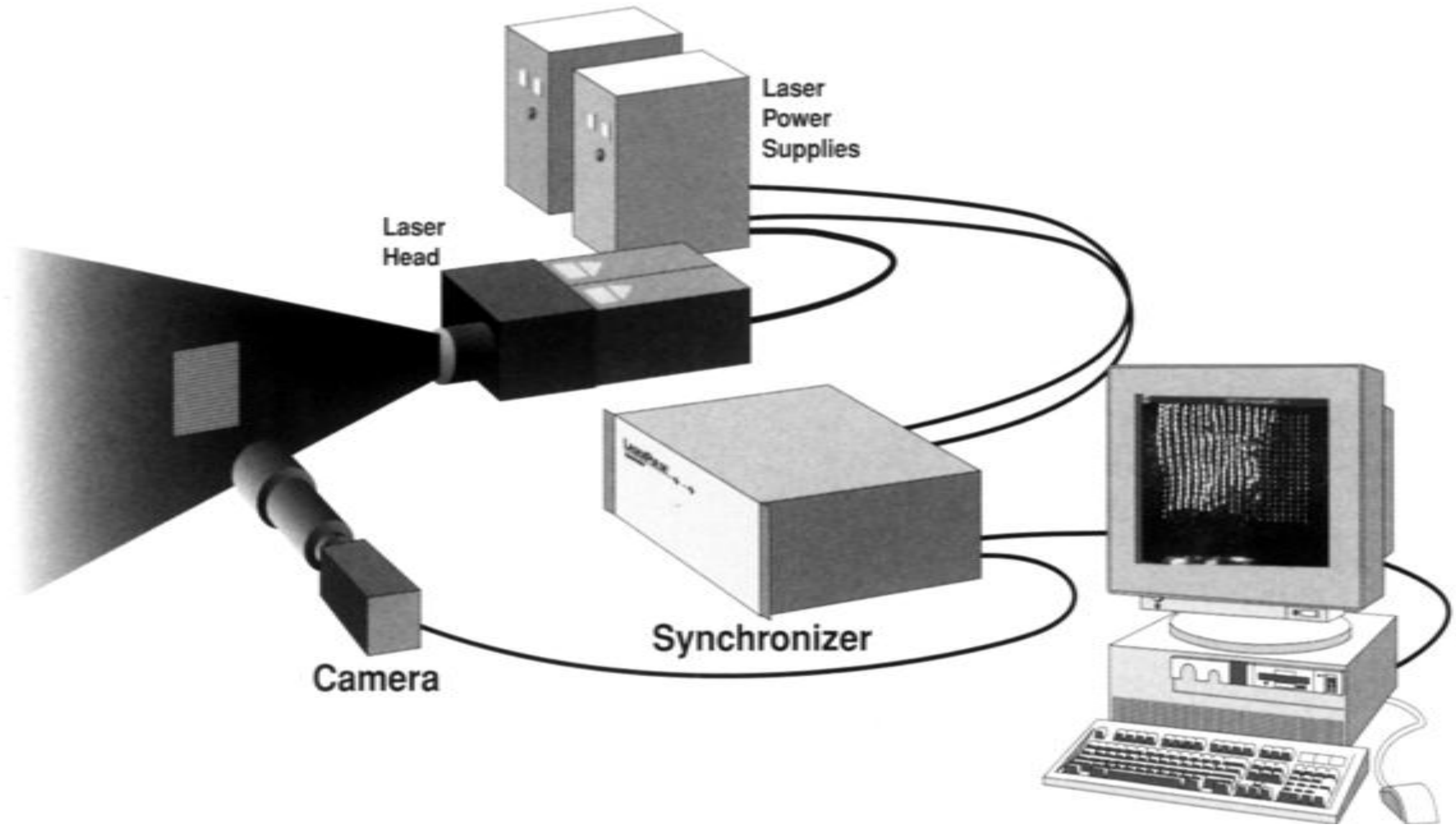
SMR

Plum Flower Mini Ring (PFMR)

CFD simulation



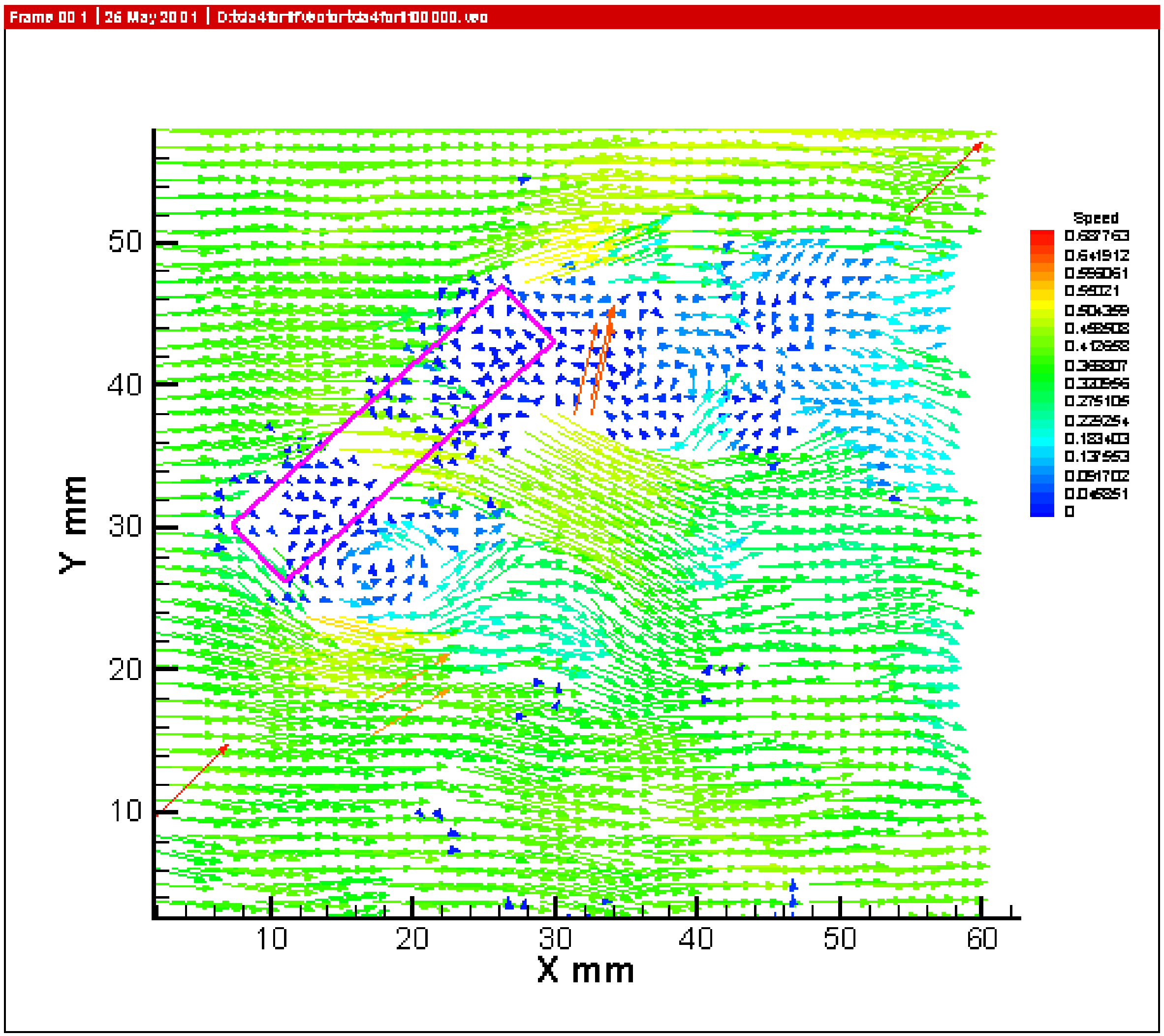
PIV Measurement



PIV（particle image velocimetry）

Velocity vector of ring packing

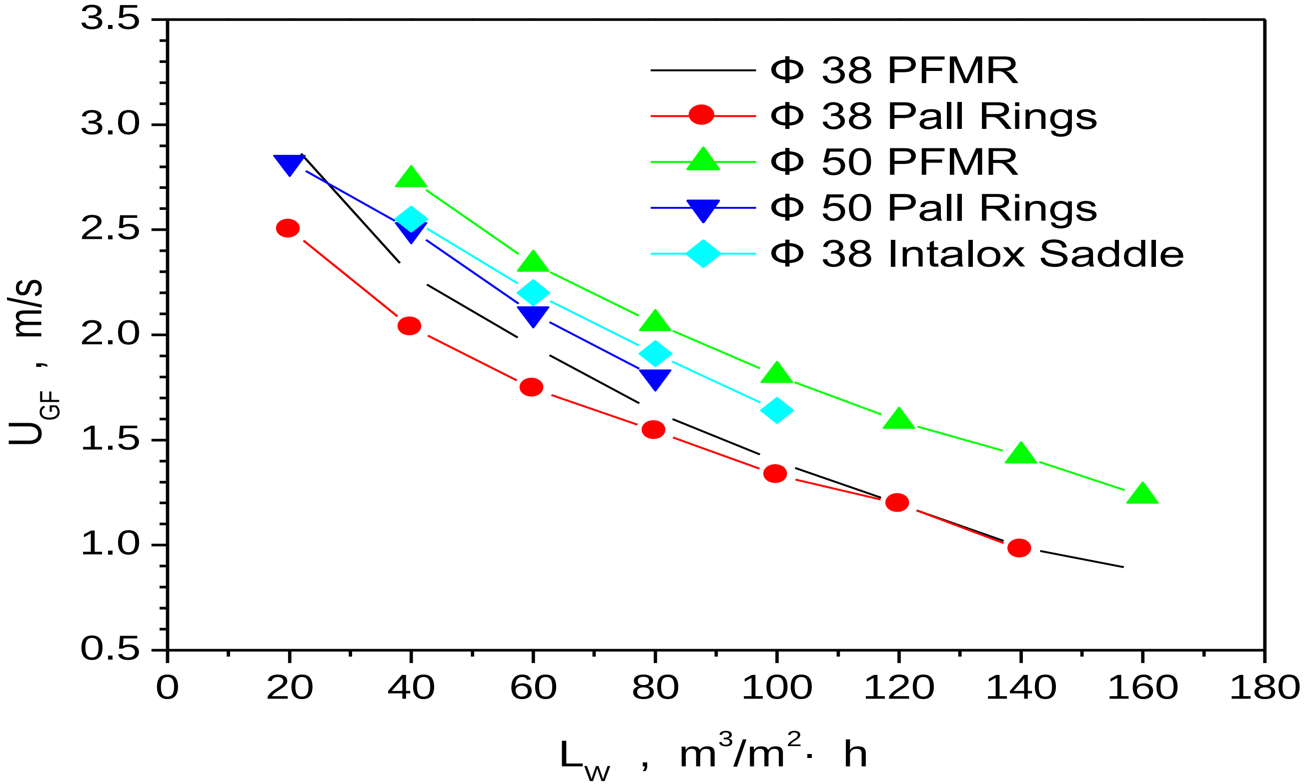
height/diameter=0.25, inclination=45



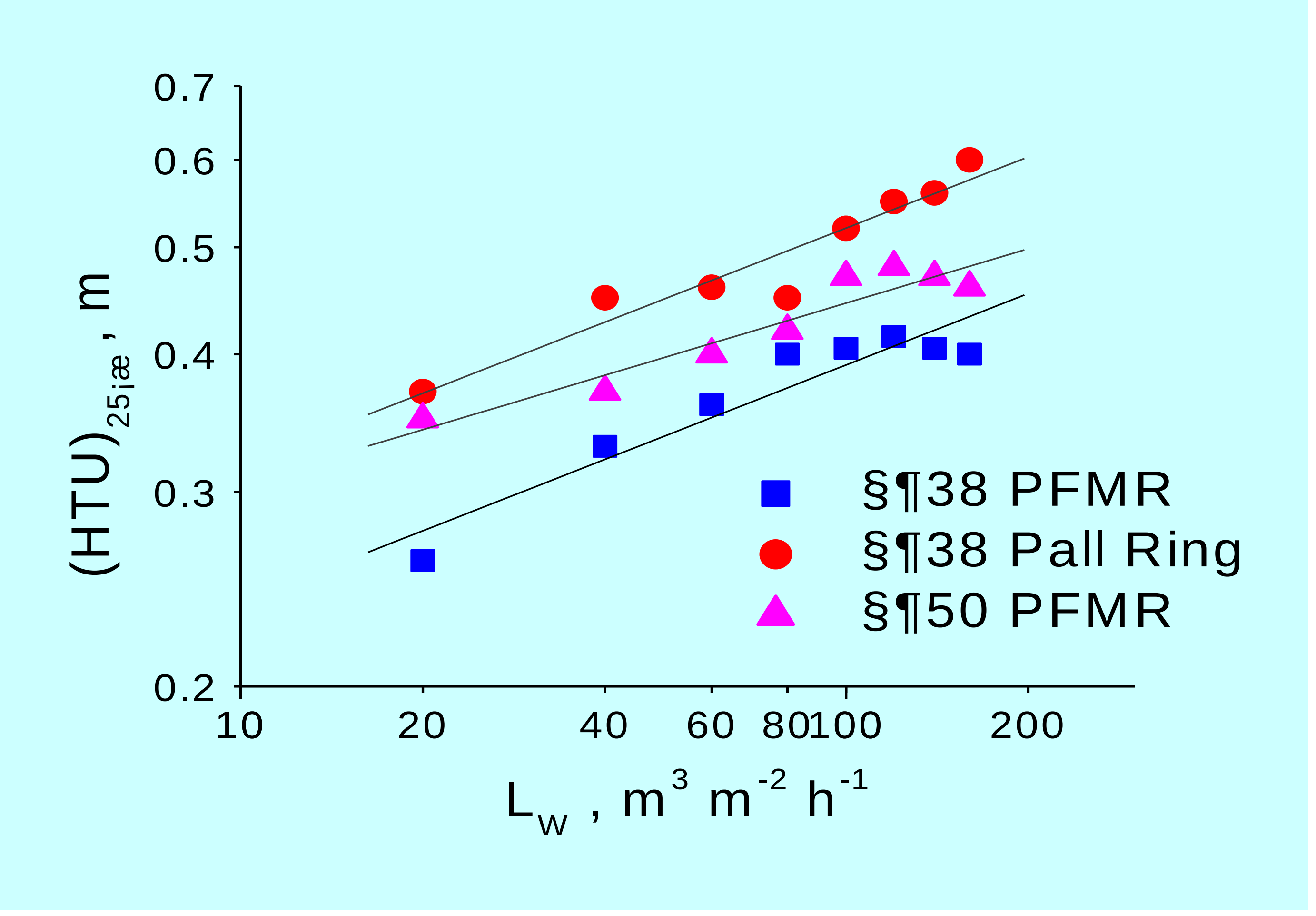
Experiment facility

Column type	Column diameter	Packing element height (m)	Packing material	Experiment system	Experiment condition
Column Ⅰ	50	0.6		alcohol and n-propyl alcohol	Total reflux, atm
Column Ⅱ	100	0.8		alcohol and water	Total reflux, atm

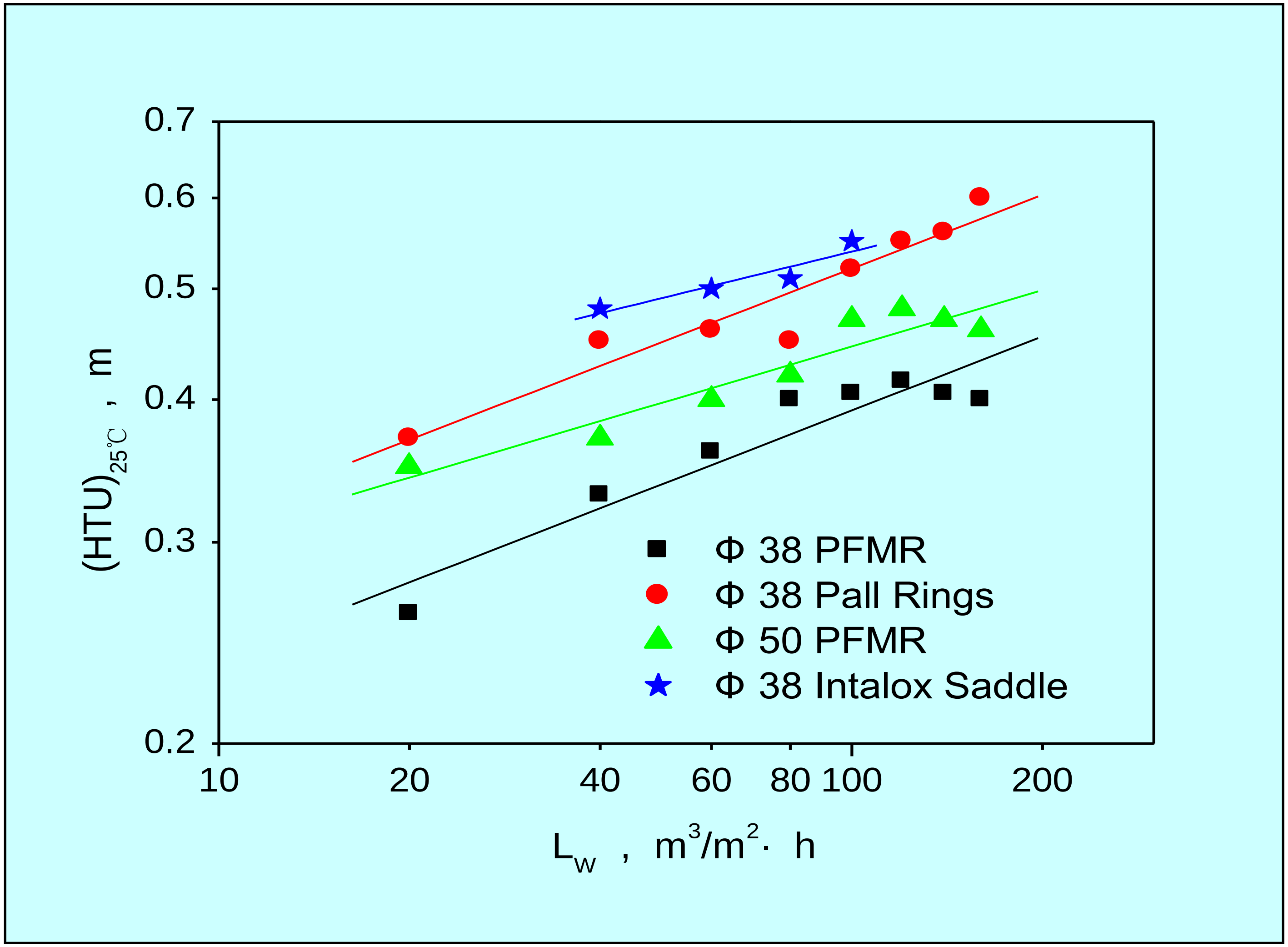
Comparison of flooding velocity among PFMR, Pall Ring & Intalox Saddle



Comparison of mass transfer between PFMR and Pall Ring

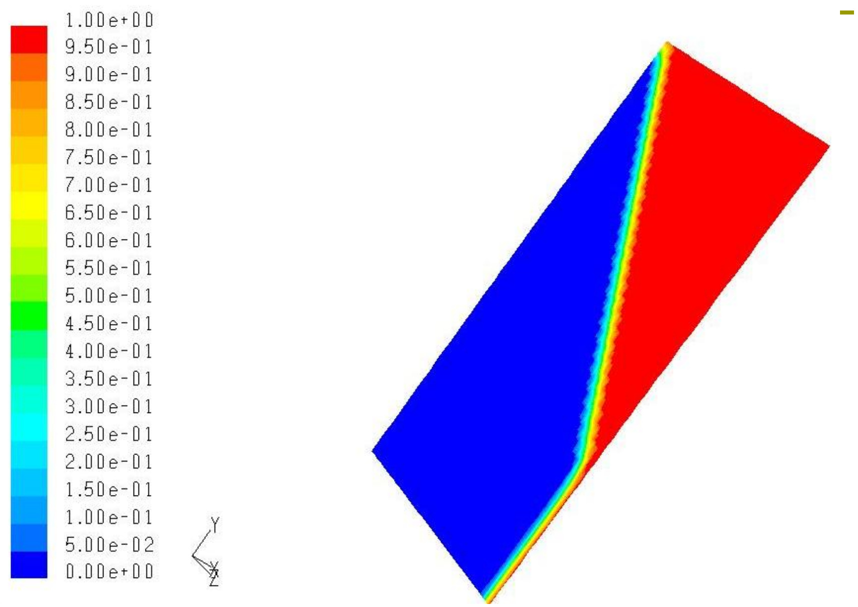


Comparison of mass transfer between PFMR, Pall Ring and Intalox Saddle

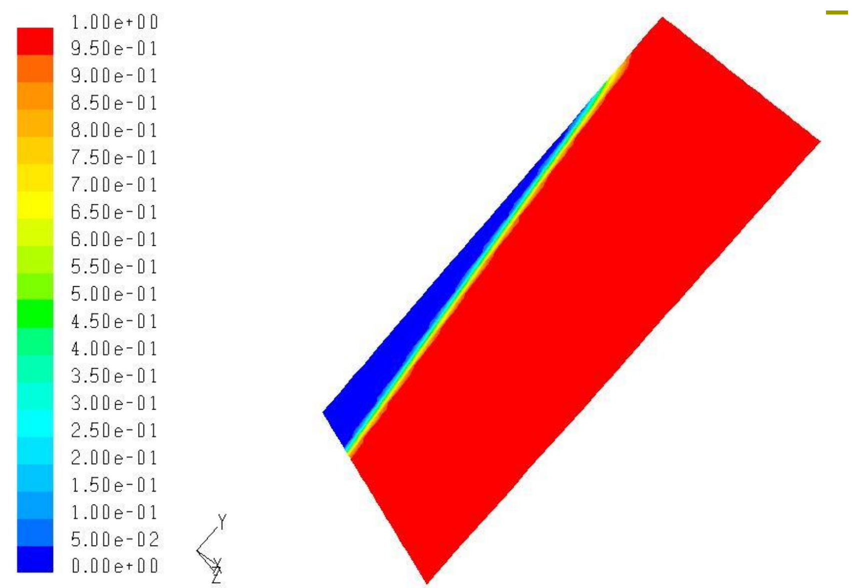


New structured packings

CFD for liquid flow on packings



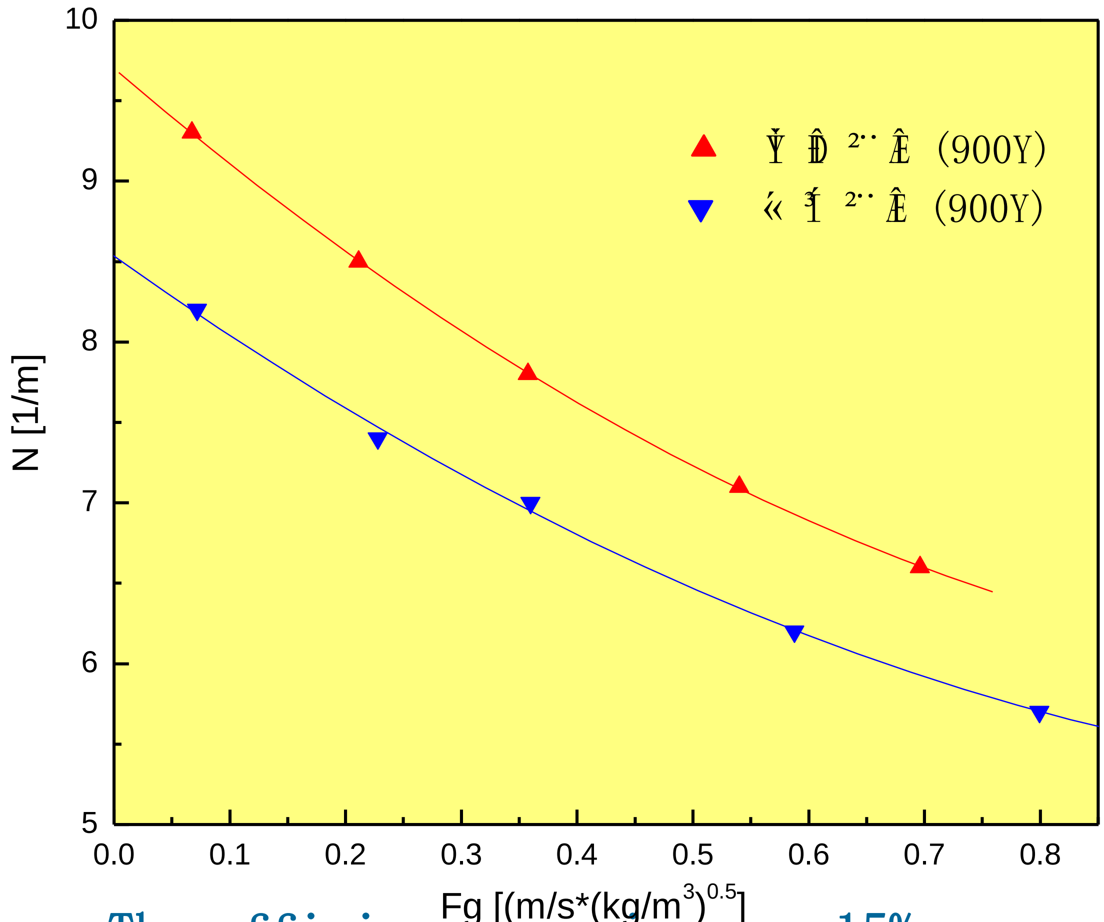
β=45^{o}



β=10^{o}

Impact of corrugation angle

Experiment results



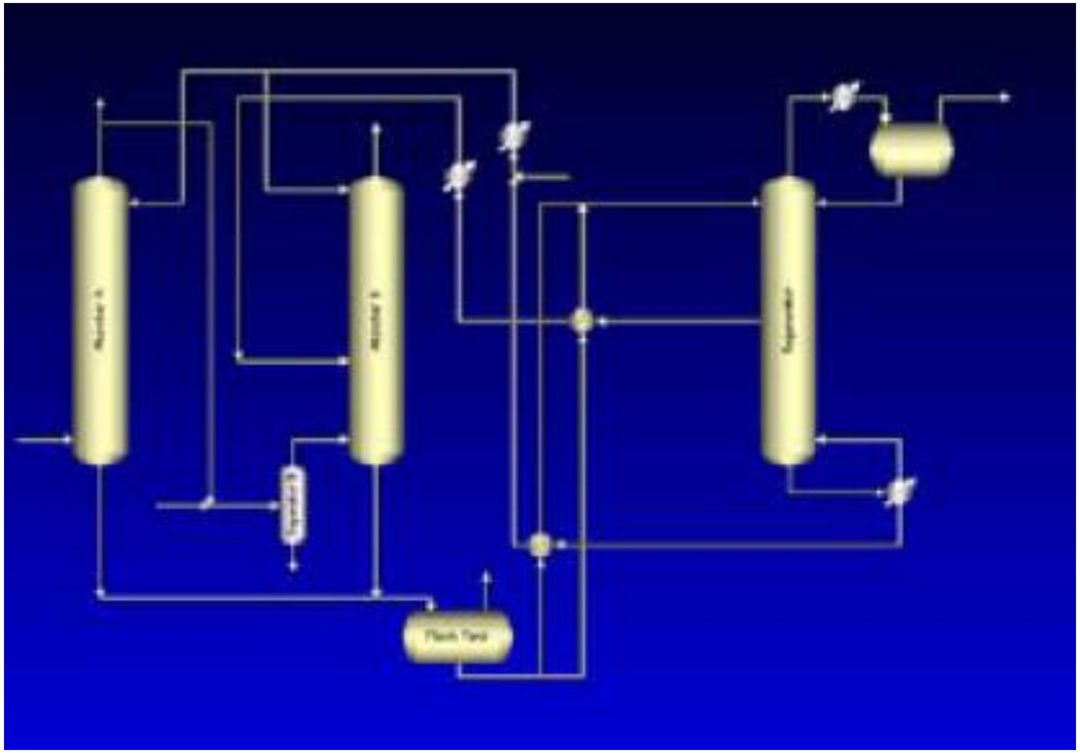
The efficiency can improve 15%

Contents

1. Background
2. Absorption Solvent
3. Mass Transfer Packings
4. **Process Simulation**

Simulation for chemical absorption processes

Solubility, kinetics and mass transfer calculation



Simulation of chemical absorption processes

Correlation of gas solubility in aqueous amine solution

Clegg-Pitzer model

$$\frac{G^E}{RT} = \frac{G^{DH}}{RT} + \frac{G^S}{RT} \qquad \ln\gamma_i = \left(\frac{\partial G^E / RT}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

$$\frac{G^{DH}}{RT} = -\frac{4A_x I_x}{\rho}\ln(1+\rho I_x^{1/2}) + \sum_c \sum_a x_c x_a B_{ca} g\left(\alpha I_x^{1/2}\right)$$

$$\frac{G^S}{RT} = x_I \sum_n x_n \sum_c \sum_a F_c F_a W_{nca} + \sum_{n>} \sum_{n'} x_n x_{n'} (A_{n'n} x_n + A_{nn'} x_{n'})$$

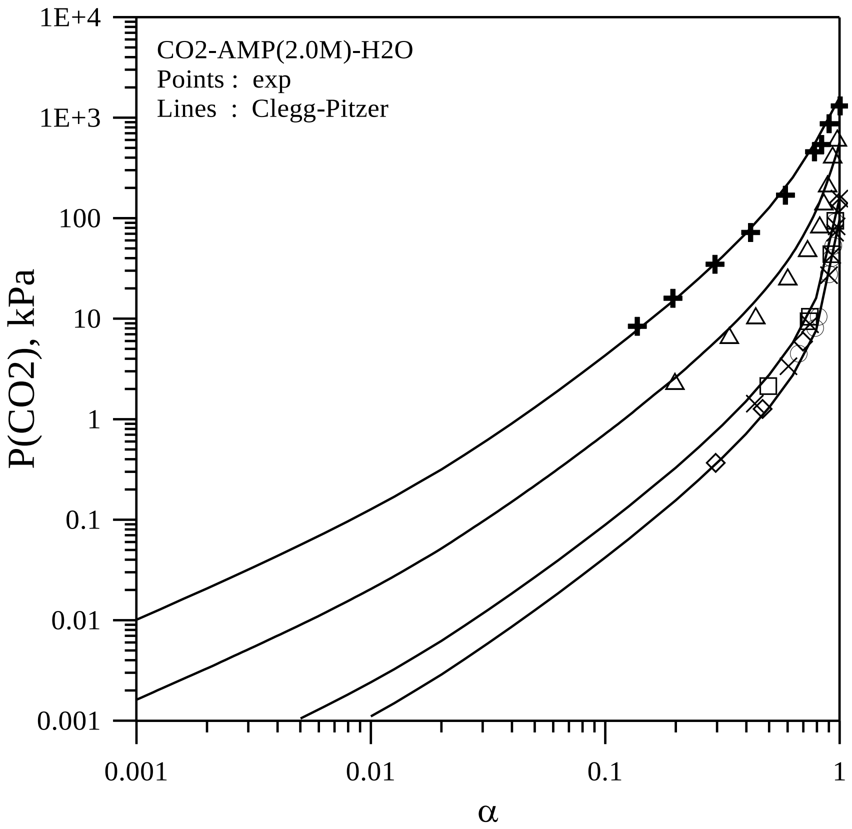
Simulation of chemical absorption processes

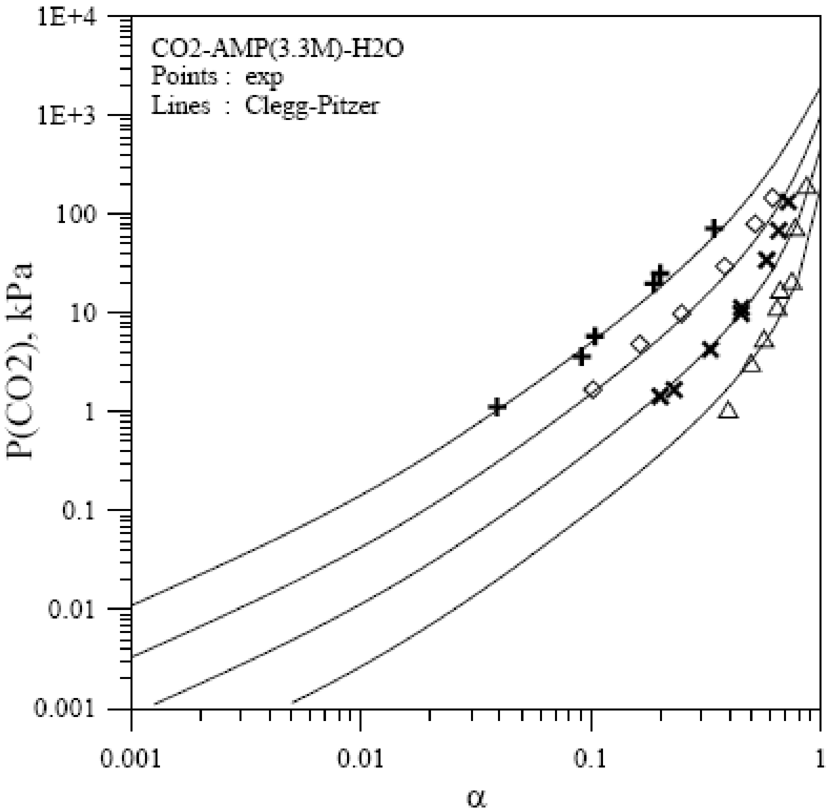
Table 1. Chemical reactions and their equilibrium constants for the system AMP-H_2O-CO_2 ($\ln K = A + B/T + C \times \ln T$)

Chemical reaction	A	*B*	*C*
$H_2O \Leftrightarrow H^+ + OH^-$	132.9	-13446.	-22.48
$AMPH^+ \Leftrightarrow AMP + H^+$	-5.525	-6382.0	0.0
$CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+$	231.5	-12092.1	-36.78
$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$	216.05	-12431.7	-35.48

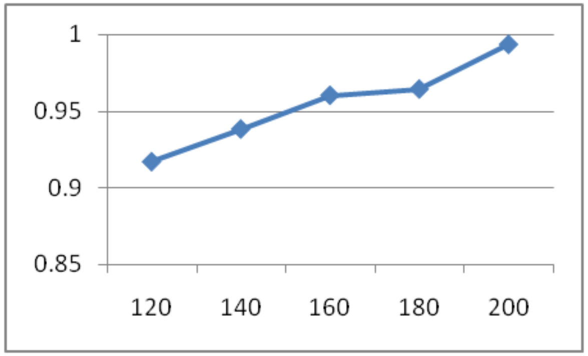
$$f_{1(G)} = f_{1(L)} = x_1 \gamma_1 H_1^0 \qquad f_{i(G)} = f_{i(L)} = x_i \gamma_i P_i^0$$

CO_2 solubility in aqueous amine solution

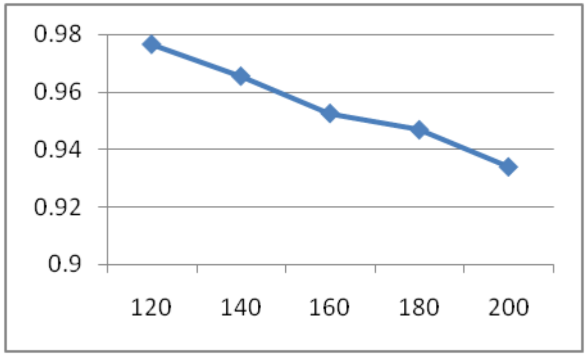




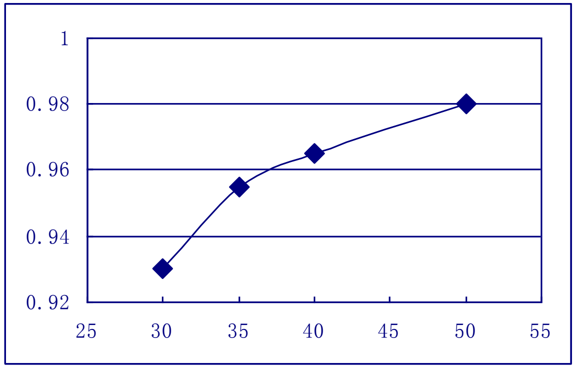
Analysis on Capture Energy Consumption



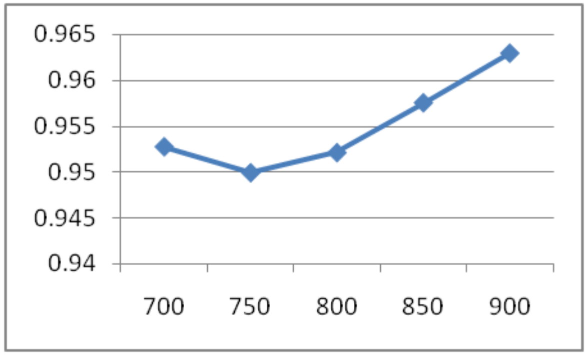
Absorption Pressure



Regeneration Pressure



Amine concentration



Solvent flowrate

Global optimization on absorption processes

Research expects

- Absorption Solvent;
  Mass transfer Packings;
  Process simulation.
- Establish a research platform on molecular design, mass transfer and process identification for CO_2 capture.
- Develop new CO_2 capture technologies with low cost.

Thanks !

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Wei Chen, Dongfang Guo, Yueyang Zhong, Que Zheng